IX.—*Contributions to the Chemistry of the Amidines.*
2-Aminothiazoles and 2-Imino-2:3-dihydrothiazoles.
2-Iminotetrahydrothiazoles and 2-Amino-4:5-
dihydrothiazoles.

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THIS investigation was undertaken with the purpose of studying the constitutions of the derivatives of such amidines as have one of the nitrogen atoms and the carbon atom of the group $-N:C:N=$ forming part of a closed chain, whilst the second nitrogen atom lies outside of the cyclic nucleus; these are referred to in the following pages as "partially cyclic" amidines. In the present paper, we describe the alkylation of some amidines belonging to the thiazole group, and the determination of the constitutions of the alkyl bases formed.

Traumann (*Annalen*, 1888, **249**, 31) found that the base formed by the action of chloroacetone on thiocarbamide, and to which he ascribed the constitution

$$\begin{array}{c} \text{CH}-\text{S} \\ || \\ \text{CMe}\cdot\text{N} \end{array} \gg \text{C}\cdot\text{NH}_2,$$

yielded on methylation the derivative

$$\begin{array}{c} \text{CH}-\text{S} \\ || \\ \text{CMe}\cdot\text{NMe} \end{array} \gg \text{C}\cdot\text{NH},$$

and that similarly the base, $\begin{array}{c} \text{CH}-\text{S} \\ || \\ \text{CPh}\cdot\text{N} \end{array} \gg \text{C}\cdot\text{NH}_2$, obtained by heating thiocarbamide with phenacyl bromide, yielded the methyl derivative,

We have methylated the bases obtained by heating methylthiocarbamide, allylthiocarbamide, and phenylthiocarbamide with chloroacetone. Traumann (*loc. cit.*) has shown that the bases formed in this manner from monosubstituted thiocarbamides, have the constitution $\begin{array}{c} \text{CH}-\text{S} \\ || \\ \text{CMe}\cdot\text{N} \end{array} \gg \text{C}\cdot\text{NHR}$. The position of the hydrogen atom, which is substituted on alkylation, is discussed later.

The methyl derivative, obtained from the base with $\text{R}=\text{CH}_3$, is identical with 2-methylimino-3:4-dimethyl-2:3-dihydrothiazole, $\begin{array}{c} \text{CH}-\text{S} \\ || \\ \text{CMe}\cdot\text{NMe} \end{array} \gg \text{C}\cdot\text{NMe}$, formed by the action of chloroacetone on *s*-dimethylthiocarbamide. To determine the constitution of the alkyl derivatives of the bases with $\text{R}=\text{C}_3\text{H}_5$ and C_6H_5 , we heated the methyl bases with concentrated hydrochloric acid at 250° in the expectation of obtaining a primary or secondary amine and the oxydihydrothiazole,

The high pressure in the tube after cooling, the evolution of hydrogen sulphide on evaporation of the mixture, and the separation of methylamine together with a less volatile primary amine (allylamine (?) and aniline respectively) from the products showed that the methyl bases had the constitutions

and that the hydrolysis had proceeded beyond the formation of the oxydihydrothiazole to, at least, partial disruption of the thiazole nucleus. In confirmation of this, it was found that 2-phenylaminothiazole, $\begin{array}{l} \text{CH} \text{---} \text{S} \\ || \quad | \\ \text{CMe} \cdot \text{N} \text{---} \text{C} \cdot \text{NHPh} \end{array}$, when hydrolysed with concentrated hydrochloric acid at 250°, yielded aniline and small quantities of ammonia, hydrogen sulphide, and carbon dioxide.

The methylation of the "partially cyclic" amidines,

has been studied by Gabriel, who methylated the bases with $\text{R} = \text{H}$ and CH_3 , and $\text{R}' = \text{H}$, and obtained the derivatives

(*Ber.*, 1889, 22, 1142, 2984), whilst Prager, who methylated the bases of this type with $\text{R} = \text{CH}_3$ and $\text{R}' = \text{C}_6\text{H}_5$ and *o*- $\text{C}_6\text{H}_4\text{Me}$ (*Ber.*, 1889, 22, 2998), obtained the derivatives

We have repeated Prager's preparations, have confirmed his results, and have extended the investigation to the methylation and ethylation of three bases in all, with $\text{R} = \text{CH}_3$ and $\text{R}' = \text{C}_6\text{H}_5$, *o*- $\text{C}_6\text{H}_4\text{Me}$, and *p*- $\text{C}_6\text{H}_4\text{Me}$. On successive oxidation and hydrolysis of the alkylated bases, we obtained in each case β -methyltaurine and the secondary base: methyl- or ethyl-aniline, *o*-toluidine, and *p*-toluidine respectively, from which follows the constitution of the alkylated bases:

Our results, together with those of Traumann, Gabriel, and Prager, show that "partially cyclic" amidines of the thiazole series, having a hydrogen atom which may be substituted directly by an alkyl group, yield on alkylation derivatives in which the alkyl is attached to the nitrogen atom of the nucleus, except when the ring is already partially reduced and R' in the formula A is an aryl group, the alkyl group in this case going to the side-chain nitrogen atom, as in B. This rule is probably of general application to the alkylation of "partially cyclic" amidines of any carbo-nitrogen heterocyclic series.

The results of alkylating "partially cyclic" amidines are in accord with those obtained by von Pechmann on methylating "mixed" amidines, if the rule of alkylation be stated in the following form:—on alkylation of an amidine, the alkyl group goes to the more negative nitrogen atom.

Von Pechmann (*Ber.*, 1895, **28**, 2362; 1897, **30**, 1780) found that on methylation of a "mixed" amidine, which might be $\text{—C} \begin{smallmatrix} \text{NHR} \\ \text{NR}' \end{smallmatrix}$ or $\text{—C} \begin{smallmatrix} \text{NR} \\ \text{NHR}' \end{smallmatrix}$, with an R, an alkyl group, or a hydrogen atom, and R', an aryl group, and in which the two nitrogen atoms must vary widely in basicity, there is obtained only one methyl derivative:

in which the methyl is attached to the same nitrogen atom as in the aryl group, that is to say, to the less basic or more negative nitrogen atom, but on methylation of a "mixed" amidine with R and R', two similar groups, as phenyl and *o*-tolyl (*Ber.*, 1895, **28**, 869) or phenyl and β -naphthyl (*Ber.*, 1897, **30**, 1783), in which the difference of the basicity of the two nitrogen atoms can be only small, a mixture of the two possible methyl derivatives is obtained.

The negative nature of a nitrogen atom in an unsaturated heterocyclic nucleus, as exemplified by the ease with which the hydrogen atom of the group —NH— is substituted by metals, is well known, as is also the increase of the basicity of cyclic compounds on reduction.

To quote one example of this: diphenyltriazole, $\text{CPh} \begin{smallmatrix} \text{N} \cdot \text{N} \\ \text{—NH—} \end{smallmatrix} \text{CPh}$ (Pinner, *Annalen*, 1897, **299**, 255), has hardly any basic properties, being soluble in dilute alkali hydroxides, but insoluble in dilute acids; whereas diphenyldihydrotriazole, $\text{CPh} \begin{smallmatrix} \text{N} \cdot \text{NH} \\ \text{—NH—} \end{smallmatrix} \text{CHPh}$ (Pinner, *loc. cit.*, p. 266), is a strong base, forming with hydrochloric, nitric, and acetic acids stable salts which are not decomposed by water.

Of the two possible "partially cyclic" amidines,

the alkyl group is in the more negative position in II, and therefore, 2-phenylimino-3:4-dimethyl-2:3-dihydrothiazole is obtained on methylation of the base

which has $R = C_6H_5$.

On the other hand, of the alkyl derivatives,

derived from Gabriel and Prager's bases,

the alkyl is probably in the more negative position in V if R = an aryl group, but in VI if R is a hydrogen atom or an alkyl group; hence Gabriel's methylated bases are of the latter, but Prager's of the former type.

The constitution of the derivative obtained on alkylation of an amidine having been determined, it is assumed usually that the constitution of the amidine is to be represented by placing a hydrogen atom in the position taken up by the alkyl. Thus, according to von Pechmann (*Ber.*, 1897, **30**, 1781), benzphenylamidine must be $\text{C}_6\text{H}_5 \cdot \text{C} \begin{smallmatrix} \text{NH} \\ \text{NHPH} \end{smallmatrix}$, because on methylation it yields the derivative

$\text{C}_6\text{H}_5 \cdot \text{C} \begin{smallmatrix} \text{NH} \\ \text{NMePh} \end{smallmatrix}$. If, however, methylation of an amidine takes place not by direct substitution, but by addition of methyl iodide and subsequent elimination of hydrogen iodide, the intermediate additive product in the formation of the methyl derivative of benzphenylamidine must be $\text{C}_6\text{H}_5 \cdot \text{CI} \begin{smallmatrix} \text{NH}_2 \\ \text{NMePh} \end{smallmatrix}$ or $\text{C}_6\text{H}_5 \cdot \text{C} \begin{smallmatrix} \text{NH}_2 \\ \text{NMePhI} \end{smallmatrix}$ (compare Beckmann and Fellrath, *Annalen*, 1893, 273, 24), which could be formed by addition of methyl iodide to an amidine only of the constitution $\text{C}_6\text{H}_5 \cdot \text{C} \begin{smallmatrix} \text{NH}_2 \\ \text{NPh} \end{smallmatrix}$.

This view of the mechanism of the alkylation of amidines is in agreement with the behaviour of ethylene- ψ -thiocarbamide and of propylene- ψ -thiocarbamide. Gabriel, having determined the constitution of their methyl derivatives (see p. 60), represented these bases by the formulæ

$$\begin{array}{c} \text{CH}_2\text{---S} \\ | \\ \text{CH}_2\cdot\text{NMe} \end{array} \rangle \text{Cl}\cdot\text{NH}_2 \quad \text{and} \quad \begin{array}{c} \text{CHMe---S} \\ | \\ \text{CH}_2\cdot\text{NMe} \end{array} \rangle \text{Cl}\cdot\text{NH}_2$$

The foregoing remarks apply only to the direct alkylation of amidines by the action of alkyl haloids at the laboratory or higher temperature with or without a solvent, and not to indirect alkylation by the action of alkyl haloids on a metallic derivative of the amidine. With the idea that methylation by the latter method might lead to the formation of the isomeric series of alkyl derivatives, we digested the silver derivatives of the 2-arylimino-5-methyltetrahydrothiazoles VIII with one molecule of methyl iodide, but without obtaining more than traces of oily products which might be the alkylated amidines, the original base being recovered almost entirely in each case.

Similarly, Bamberger and Lorenzen (*loc. cit.*, p. 282) found that only very small amounts of 1:2:5-trimethylbenzimidazole were

formed by the action of methyl iodide on the silver derivative of 2:5-dimethylbenzimidazole, whilst Meldola, Eyre, and Lane (*Trans.*, 1903, **83**, 1185) obtained the same alkyl derivatives from ethenyldi-aminonaphthalenes by the direct and the indirect methods of alkylation, but in much the poorer yields by the latter process. We suggest that in reality no alkylation of these amidines takes place by the indirect method, the small amounts of alkyl derivatives formed being due to interaction of the alkyl iodide with the liberated amidine, especially as the best yields by the indirect method appear to be obtained when, as in the experiments of Meldola, Eyre, and Lane (*loc. cit.*, p. 1193), an excess of the alkyl haloid is employed.

On the other hand, 2-acetylimino-3:4-dimethyl-2:3-dihydrothiazole, $\begin{array}{c} \text{CH} \text{---} \text{S} \\ | \quad \diagup \\ \text{CMe} \cdot \text{NMe} \end{array} > \text{C:N} \cdot \text{N} \cdot \text{Ac}$, is formed in good yield by the indirect method from the acetyl derivative of 2-amino-4-methylthiazole, as was 2-acetylimino-5-phenyl-3-methyl-2:3-dihydrothiodiazole,

from 2-amino 5-phenylthiodiazole, studied by Young and Eyre (*Trans.*, 1901, **79**, 54), whereas attempts to methylate the last substance by the direct method met with no success. It may be that the greatly diminished basicity of the nitrogen atom of the side-chain consequent on the introduction of the acetyl group causes isomeric change to take place:

the hydrogen atom being less labile when attached to the less negative atom, the subsequent direct substitution, on treatment of the silver derivative with methyl iodide,

being due to the increased acidity of the molecule.

EXPERIMENTAL.

2-Aminothiazoles and 2-Imino-2:3-dihydrothiazoles.

2-Anilino-4-methylthiazole was prepared by Hantzsch and Weber (*Ber.*, 1887, **20**, 3130) by the action of aniline on 2-hydroxy-4-methylthiazole, and was found by these authors to melt at 117°. Traumann (*loc. cit.*), who prepared the base by acting on phenylthiocarbamide with chloroacetone, found it to melt at 115°. On repeating the

preparation by Traumann's method, we obtained a substance which crystallised from dilute alcohol in long needles and melted at 117—118°. When boiled with acetic anhydride and sodium acetate, the base formed an *acetyl* derivative, which was readily soluble in alcohol or benzene, but only moderately so in light petroleum; from the last solvent it crystallised, on slow evaporation, in clusters of soft, white, silky, matted needles which melted at 114·5°.

0·1655 gave 17·0 c.c. moist nitrogen at 16° and 755 mm. $N = 11·95$.
 $C_{10}H_9N_2S \cdot C_2H_5O$ requires $N = 12·07$ per cent.

2-Phenylimino-3 : 4-dimethyl-2 : 3-dihydrothiazole, $\begin{array}{c} \text{CH} \text{---} \text{S} \\ | \quad \quad | \\ \text{CMe} \cdot \text{NMe} \end{array} > \text{C} : \text{NPh}.$

2-Anilino-4-methylthiazole was heated with methyl iodide and methyl alcohol in a closed vessel for one hour in the water-bath, and the product, after being diluted with water and boiled to expel the methyl alcohol, made alkaline and extracted with benzene; the oily residue obtained on drying and distilling the benzene residue was allowed to solidify slowly in a desiccator over soda-lime. The base prepared in this manner was moderately soluble in warm light petroleum, from its solution in which it separated in small, white crystals melting at 65—66°.

0·1458 gave 17·4 c.c. moist nitrogen at 14·5° and 755 mm. $N = 13·93$.
 $C_{11}H_{12}N_2S$ requires $N = 13·72$ per cent.

The *platinichloride*, formed by adding platinic chloride to the solution of the base in warm dilute hydrochloric acid, crystallised from the solution on cooling, and after being dried at 105° melted at 189—190°.

0·2446 gave 0·0584 Pt. $\text{Pt} = 23·88$.
 $(C_{11}H_{12}N_2S)_2, H_2PtCl_6$ requires $\text{Pt} = 23·83$ per cent.

Hydrolysis of 2-Phenylimino-3 : 4-dimethyl-2 : 3-dihydrothiazole.

The methylated base was heated with concentrated hydrochloric acid in a sealed tube at 245—250° for four and a half hours. After concentration on the water-bath, during which operation considerable quantities of hydrogen sulphide were evolved, an excess of potassium hydroxide was added and the product distilled in a current of steam, any alkaline vapours which passed through the receiver being retained by an acid trap. The distillate, after acidification and concentration, was again made alkaline and boiled in a reflux apparatus until no alkaline vapours could be detected on removal of the hydrochloric acid trap. The residual liquid in the boiling flask gave the *isonitrile*

reaction for primary amines and the bleaching powder reaction for aniline, whilst the solution from the hydrochloric acid trap gave only the first of these two reactions, but when made alkaline smelt strongly of methylamine. In one experiment, a small amount of a white, solid substance separated from the distillate; it melted at 78° and was possibly 2-oxy-3:4-dimethyl-2:3-dihydrothiazole.

The hydrochloride of this base was formed by gradually adding 1 mol. of chloroacetone to 1 mol. of allylthiocarbamide; as the reaction takes place with considerable development of heat, it was necessary to cool the mixture with water. The cold product was treated with aqueous potassium hydroxide, and the solid thus obtained recrystallised from light petroleum, when it formed long, white, silky needles. The base, which was observed to have a slight odour resembling that of thyme, melted at $40-41^{\circ}$.

0.2572 gave 40.9 c.c. moist nitrogen at 15° and 753 mm. $\text{N} = 18.44$.

0.1780 „ 0.2640 BaSO_4 . $\text{S} = 20.66$.

$\text{C}_7\text{H}_{10}\text{N}_2\text{S}$ requires $\text{N} = 18.18$; $\text{S} = 20.78$ per cent.

The *acetyl* derivative, formed by boiling 2-allylamino-4-methylthiazole with acetic anhydride, was obtained as an oil which solidified slowly to a crystalline mass; it was readily soluble in benzene, but only moderately so in light petroleum, from which it crystallised in thin, square plates. It melted at $36-37^{\circ}$ and had, especially before recrystallisation, an odour resembling that of impure acetamide.

0.2590 gave 0.3040 BaSO_4 . $\text{S} = 16.12$.

$\text{C}_7\text{H}_9\text{N}_2\text{S} \cdot \text{C}_2\text{H}_3\text{O}$ requires $\text{S} = 16.33$ per cent.

The hydriodide formed by heating 2-allylamino-4-methylthiazole with methyl iodide and methyl alcohol in a closed vessel at 100° separated from the mixture after some days in almost colourless, large, prismatic plates. When dissolved in a small quantity of alcohol, in which it was readily soluble, and precipitated by addition of ether, the salt was obtained as a white, crystalline meal, which melted at $116-117^{\circ}$.

0.2035 gave 0.1616 AgI . $\text{I} = 42.94$.

$\text{C}_8\text{H}_{12}\text{N}_2\text{S} \cdot \text{HI}$ requires $\text{I} = 42.89$ per cent.

On treatment of the hydriodide with potassium hydroxide in concentrated aqueous solution, extraction of the product with benzene, and evaporation of the extract, the free base was obtained as a slightly red, viscid oil possessing a characteristic odour; it was readily soluble in dilute acids, and formed a crystalline *platinichloride*, which dissolved to only a slight extent in hot dilute hydrochloric acid.

Hydrolysis of 2-Allylimino-3:4-dimethyl-2:3-dihydrothiazole.

The methylated base was heated with concentrated hydrochloric acid in a sealed tube at 230—240° for five hours. The product was concentrated, made alkaline, and distilled in a current of steam; the distillate was treated in the same manner as that obtained by the hydrolysis of 2-phenylimino-3:4-dimethyl-2:3-dihydrothiazole. Both the residual liquid from the reflux apparatus and the solution from the hydrochloric acid trap gave the *isonitrile* reaction, showing that the hydrolysis had resulted in the formation of two primary amines.

2-Acetylimino-4-methyl-2:3-dihydrothiazole,

2-Amino-4-methylthiazole hydrochloride was prepared by the action of chloroacetone on thiocarbamide (Traumann, *loc. cit.*), and the base liberated by addition of concentrated aqueous potassium hydroxide and extracted with benzene. On evaporation of the extract, there was obtained a slightly pink oil, which, when cooled over calcium chloride in a desiccator, solidified to a white, slightly hygroscopic solid melting at 42°. The acetyl derivative, formed by boiling the anhydrous base with 1 mol. of acetic anhydride in a reflux apparatus, is moderately soluble in warm water, from which it separates on cooling in shining, colourless crystals. The melting point was found to be 134°, as given by Traumann.

On addition of 1 mol. of silver nitrate and 1 mol. of ammonia in aqueous solution to its solution in alcohol, the acetyl compound formed a *silver* derivative as a dense, white precipitate, which, after being well washed and dried at 100°, was fairly stable to light.

0.1962 gave 0.0809 Ag. Ag = 41.23.

$\text{C}_4\text{H}_4\text{N}_2\text{SAg} \cdot \text{C}_2\text{H}_5\text{O}$ requires Ag = 41.03 per cent.

When heated with 1 mol. of methyl iodide in methyl-alcoholic solution in a closed vessel at 100°, the silver derivative forms 2-acetylimino-3:4-dimethyl-2:3-dihydrothiazole,

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product recrystallised from hot dilute alcohol. The base obtained in this manner crystallised in needles and melted at 117° (Prager, *loc. cit.*).

0.1673 gave 0.2044 BaSO_4 . $\text{S} = 16.79$.

0.1577 „ 19.6 c.c. moist nitrogen at 11.5° and 755 mm. $\text{N} = 14.71$.

$\text{C}_{10}\text{H}_{12}\text{N}_2\text{S}$ requires $\text{S} = 16.67$; $\text{N} = 14.58$ per cent.

The base formed a picrate, which crystallised from dilute alcohol in rough, yellow needles and melted at 154° .

0.1378 gave 20.7 c.c. moist nitrogen at 19° and 725 mm. $\text{N} = 16.46$.

$\text{C}_{10}\text{H}_{12}\text{N}_2\text{S}, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires $\text{N} = 16.63$ per cent.

When shaken with acetic anhydride, the base dissolved with slight development of heat, forming a clear solution; after some time, the mixture was dissolved in ether, and the ethereal solution was washed with aqueous potassium carbonate, dried, and distilled on the water-bath. The residual oil gradually solidified to a crystalline mass which melted at 47° .

0.1808 gave 0.4069 CO_2 and 0.0993 H_2O . $\text{C} = 61.38$; $\text{H} = 6.10$.

0.1552 „ 0.1557 BaSO_4 . $\text{S} = 13.79$.

$\text{C}_{10}\text{H}_{11}\text{N}_2\text{S} \cdot \text{C}_2\text{H}_5\text{O}$ requires $\text{C} = 61.54$; $\text{H} = 5.98$; $\text{S} = 13.68$ per cent.

The acetyl derivative was readily soluble in alcohol, ether, or benzene, less so in light petroleum, and separated from its solutions as an oil, which rapidly solidified on addition of a small quantity of the crystalline substance.

When dissolved in alcohol and poured into an alcoholic solution of silver nitrate, the base formed the *silver* derivative, $\text{C}_{10}\text{H}_{11}\text{N}_2\text{SAg}$, which was obtained as a white precipitate. After being washed with dilute alcohol and dried at 90° , the silver derivative detonated when heated on a piece of porcelain over the Bunsen flame, whilst when heated in a capillary tube it blackened and commenced to melt at 130° .

0.2473 gave 0.0890 Ag. $\text{Ag} = 35.99$.

$\text{C}_{10}\text{H}_{11}\text{N}_2\text{SAg}$ requires $\text{Ag} = 36.08$ per cent.

With the object of obtaining possibly a methyl base isomeric with that prepared by Prager, the silver derivative was warmed with 1 mol. of methyl iodide in methyl-alcoholic solution and the product evaporated and shaken with benzene. The base obtained on evaporation of the benzene solution was converted into its picrate, which crystallised in rough, yellow needles, melted at 154° , and gave analytical results agreeing with those required by the picrate of 2-phenylimino-5-methyltetrahydrothiazole.

0.1279 gave 18.7 c.c. moist nitrogen at 17° and 756 mm. N = 16.86.

$C_{10}H_{12}N_2S, C_6H_3O_7N_3$ requires N = 16.63 per cent.

$C_{10}H_{11}N_2SMe, C_6H_3O_7N_3$ „ N = 16.09 „ „

2-Phenylmethylamino-5-methyl-4 : 5-dihydrothiazole,

As the action of methyl iodide on the silver derivative did not lead to the formation of a methyl base, 2-phenylimino-5-methyltetrahydrothiazole was heated with 1 mol. of methyl iodide in methyl-alcoholic solution in a closed vessel at 100°. The base was mixed also with an excess of methyl iodide, and the mixture was allowed to stand overnight in a flask cooled by ice-water (Prager, *loc. cit.*, p. 2997). By these two methods, the same methyl base was obtained as an oil, readily soluble in alcohol, ether, benzene, or dilute acids.

The *platinichloride* of the methyl base crystallised in salmon-coloured, nodular aggregates of plates and melted at 184°.

A.* 0.4758 gave 0.1132 Pt. Pt = 23.79.

B. 0.3254 „ 0.0775 Pt. Pt = 23.81.

$(C_{11}H_{14}N_2S)_2, H_2PtCl_6$ requires Pt = 23.69 per cent.

The *picrate* of the methyl base melted under boiling water, in which it was slightly soluble, crystallising on cooling in soft, yellow needles; it dissolved readily in alcohol, from which, on dilution, it crystallised in clusters of yellow needles. It melted at 114—115°; Prager gives its melting point as 125°.

A. 0.1180 gave 17.1 c.c. moist nitrogen at 18° and 740 mm. N = 16.28.

B. 0.1525 „ 21.8 „ „ „ 19° „ 751 mm. N = 16.23.

$C_{11}H_{14}N_2S, C_6H_3O_7N_3$ requires N = 16.09 per cent.

2-Phenylethylamino-5-methyl-4 : 5-dihydrothiazole,

2-Phenylimino-5-methyltetrahydrothiazole was heated with 1 mol. of ethyl iodide in ethyl-alcoholic solution in a closed vessel at 100° and the product boiled with a small quantity of water, made alkaline, and extracted with benzene. On evaporation of the benzene, the *ethyl* base was obtained as an oil, which was readily soluble in alcohol or ether, less so in light petroleum, and only sparingly so in water, and had the peculiar odour characteristic of the group of compounds. On addition

* The analyses A and B given for the platinichloride and picrate are for the salts of the base prepared by the first and second methods of methylation respectively.

of platinic chloride to its solution in dilute hydrochloric acid, the base formed the *platinichloride*, which separated as a reddish-yellow, crystalline powder and melted and decomposed at 156°.

0·6488, dried at 105°, gave 0·1488 Pt. Pt = 22·93.

(C₁₂H₁₆N₂S)₂·H₂PtCl₆ requires Pt = 22·94 per cent.

Formation of β-Methyltaurine from 2-Phenylethylamino-5-methyl-4:5 dihydrothiazole.

The ethyl base was oxidised with potassium chlorate in slightly warm hydrochloric acid, and the product evaporated to dryness and extracted with a mixture of alcohol and ether. The residue from this extract was heated with concentrated hydrochloric acid in a sealed tube at 150—200°, and the solution filtered from tarry matters and evaporated to dryness. On extracting the dried product with absolute alcohol, a white residue was obtained, which, after recrystallisation from 90 per cent. alcohol, separated from a small quantity of warm water in transparent, rhombic plates and agreed in its other properties with those of β-methyltaurine as described by Gabriel (*Ber.*, 1889, 22, 2984). When powdered and heated in a capillary tube, β-methyltaurine melts at 284—285°.

0·1732 gave 0·1638 CO₂ and 0·1015 H₂O. C = 25·79 ; H = 6·51.

0·1845 „ 0·3143 BaSO₄. S = 23·39.

0·1936 „ 17·5 c.c. moist nitrogen at 17° and 742 mm. N = 10·24.
NH₂·CH₂·CHMe·SO₃H requires C = 25·90 ; H = 6·48 ; N = 10·07 ;
S = 23·02 per cent.

s-p-Tolylallylthiocarbamide, C₆H₄Me·NH·CS·NH·C₃H₅.

This substance was prepared by boiling *p*-toluidine with a slight excess of allylthiocarbimide in alcoholic solution in a reflux apparatus. On removal of the alcohol and excess of the thiocarbimide by distillation in a current of steam, the product separated as a heavy oil, which solidified on cooling and, after purification by repeated crystallisation from dilute alcohol, was obtained in nodular aggregates of almost colourless needles which melted at 98°.

0·2011 gave 0·2304 BaSO₄. S = 15·75.

C₁₁H₁₄N₂S requires S = 15·53 per cent.

$$\begin{array}{c} \text{CHMe}\cdot\text{S} \\ | \\ \text{CH}_2\cdot\text{NH} \end{array} > \text{C}:\text{N}\cdot\text{C}_7\text{H}_7.$$
$$\begin{array}{c} \text{CHMe}\cdot\text{S} \\ | \\ \text{CH}_2-\text{N} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}\cdot\text{NMe}\cdot\text{C}_7\text{H}_7.$$

On shaking 2-*p*-tolylimino-5-methyltetrahydrothiazole with slightly more than one mol. of methyl iodide, the mixture became warm and changed to a clear liquid which gradually solidified. The product was boiled with a small quantity of water to free it from the excess of methyl iodide, made alkaline, and extracted with ether. The

methyl base, which was obtained as an oil on evaporating the ethereal extract, dissolved readily in dilute hydrochloric acid, alcohol, ether, or benzene, and had the characteristic odour of the 2-amino-4:5-dihydrothiazoles.

The *platinichloride* melted and decomposed at 110°.

0.2213 gave 0.0513 Pt. Pt = 23.18.

(C₁₂H₁₆N₂S)₂.H₂PtCl₆ requires Pt = 22.94 per cent.

Oxidation of 2-p-Tolylmethylamino-5-methyl-4:5-dihydrothiazole.

The *p*-tolylmethylamino-base was oxidised with potassium chlorate and hydrochloric acid, and the product treated as described under the oxidation of the phenylethylamino-base. The final residue, after extraction with absolute alcohol, crystallised from water in transparent plates, melted at 284—285°, and on analysis gave numbers agreeing with those required for β-methyltaurine.

0.1821 gave 0.3088 BaSO₄. S = 23.32.

C₃H₉O₃NS requires S = 23.02 per cent.

The absolute alcoholic extract was evaporated with hydrochloric acid, treated with an excess of aqueous potassium hydroxide, and distilled in a current of steam. On addition of hydrochloric acid and platinic chloride to the distillate, the *platinichloride* of methyl-*p*-toluidine separated as a red, crystalline powder, which was dried at 110°.

0.4109 gave 0.1222 Pt. Pt = 29.74.

(C₆H₄Me·NHMe)₂.H₂PtCl₆ requires Pt = 29.91.

2-p-Tolylethylamino-5-methyl-4:5-dihydrothiazole,

2-p-Tolylimino-5-methyltetrahydrothiazole was heated with slightly more than one mol. of ethyl iodide in ethyl-alcoholic solution in a closed vessel for one hour at 100°, and the product boiled with water, made alkaline and extracted with ether. The ethyl base was obtained, on evaporation of the ethereal solution, as an oil which was easily soluble in alcohol, benzene, or dilute acids.

The *platinichloride* separated from its solution in warm dilute hydrochloric acid in orange-coloured crystals, which melted and decomposed at 189—190°.

0.6832 gave 0.1505 Pt. Pt = 22.03.

(C₁₃H₁₈N₂S)₂.H₂PtCl₆ requires Pt = 22.21 per cent.

Oxidation of 2-p-Tolyethylamino-5-methyl-4:5-dihydrothiazole.

The *p*-tolylethylamino-base was oxidised with potassium chlorate and dilute hydrochloric acid, and the product hydrolysed with concentrated hydrochloric acid at 160—200°. The residue obtained on evaporation was extracted with absolute alcohol and recrystallised from water, when it formed transparent plates and melted at 284—285° (β -methyltaurine).

0.1932 gave 0.3286 BaSO₄. S = 23.38.

C₃H₉O₃NS requires S = 23.02 per cent.

The alcoholic extract yielded the *platinichloride* of ethyl-*p*-toluidine.

0.2336 gave 0.0666 Pt. Pt = 28.51.

(C₆H₄Me·NH₂)₂·H₂PtCl₆ requires Pt = 28.68 per cent.

This base was prepared according to Prager's directions (*loc. cit.*, p. 2999) from *s*-o-tolylallylthiocarbamide; it crystallised in small plates and melted at 126°.

0.1699 gave 0.1941 BaSO₄. S = 15.71.

C₁₁H₁₄N₂S requires S = 15.53 per cent.

On addition of silver nitrate to its solution in alcohol, the base formed the *silver* derivative as a white precipitate, which was washed and dried at 105°.

0.9561 gave 0.3289 Ag. Ag = 34.40.

C₁₁H₁₃N₂SAg requires Ag = 34.49 per cent.

The *acetyl* derivative, C₁₁H₁₃N₂S·C₂H₃O, was prepared by boiling the base with acetic anhydride and shaking the product with water; it crystallised from light petroleum in stout prisms, melted at 58°, and was easily soluble in benzene, alcohol, ether, or acetone, but only sparingly so in light petroleum.

0.1529 gave 0.3522 CO₂ and 0.0897 H₂O. C = 62.82; H = 6.52.

0.2137 „ 0.2029 BaSO₄. S = 13.05.

C₁₃H₁₆ON₂S requires C = 62.90; H = 6.45; S = 12.90 per cent.

The acetyl derivative dissolved unchanged in cold dilute hydrochloric acid from its solution, in which it was precipitated unchanged on addition of aqueous sodium hydroxide, but when boiled with the dilute acid it was hydrolysed, and the precipitate obtained on addition of the alkali hydroxide consisted of the parent base melting at 126°.

2-o-Tolylmethylamino-5-methyl-4:5-dihydrothiazole,

This substance was obtained as an oil by shaking 2-o-tolylimino-5-methyltetrahydrothiazole with methyl iodide and liberating the methyl base with aqueous potassium hydroxide. The *platinichloride* melted and decomposed at about 200°.

0.5318 gave 0.1217 Pt. Pt = 22.88.

(C₁₂H₁₆N₂S)₂.H₂PtCl₆ requires Pt = 22.94 per cent.

On oxidising the base with potassium chlorate and hydrochloric acid and hydrolysing the product with concentrated hydrochloric acid at 150—200°, we obtained, as did Prager, β -methyltaurine melting at 284—285°.

0.3044 gave 0.5106 BaSO₄. S = 23.31.

C₃H₉O₃NS requires S = 23.02 per cent.

2-o-Tolyylethylamino-5-methyl-4:5-dihydrothiazole,

The hydriodide of this base was formed by heating 2-o-tolylimino-5-methyltetrahydrothiazole with ethyl iodide and ethyl alcohol in a closed vessel at 100°. When liberated by means of potassium hydroxide, the base was obtained as an oil which had the characteristic odour and dissolved readily in alcohol, ether, benzene, or dilute acids. The *platinichloride* formed orange-red crystals which melted and decomposed at 203°.

0.7959 gave 0.1764 Pt. Pt = 22.17.

(C₁₃H₁₈N₂S)₂.H₂PtCl₆ requires Pt = 22.21 per cent.

The base was oxidised with potassium chlorate and hydrochloric acid, the oxidation product hydrolysed with concentrated hydrochloric acid, and the residue obtained by evaporation extracted with absolute alcohol. The part insoluble in absolute alcohol was β -methyltaurine, as after recrystallisation from 90 per cent. alcohol it melted at 284—285°.

0.1587 gave 0.1499 CO₂ and 0.0945 H₂O. C = 25.76 ; H = 6.62.

0.2173 „ 19.2 c.c. moist nitrogen at 16° and 754 mm. N = 10.22.

C₃H₉O₃NS requires C = 25.90 ; H = 6.48 ; N = 10.07 per cent.

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The absolute alcoholic extract yielded the *platinichloride* of ethyl-*o*-toluidine.

0.2786 gave 0.0800 Pt. Pt = 28.70.

$(C_6H_4Me \cdot NH_2)_2, H_2PtCl_6$ requires Pt = 28.68 per cent.

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